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Activation Volumes and the Mechanism of Aquation of *trans*-$CoN_4X_2^+$ and *trans*-$Co(NH_3)_4CN(X)^+$ Complexes

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The pressure, temperature and pH dependencies of the rate of aquation of a range of trans-*complexes with the general formula* $CoN_4X_2^+$ *were studied where* $X = Cl$ *and* $N_4 \equiv (NH_3)_4$; $(en)_2$; *R,S-(2,3,2-tet); RR,SS-(2,3,2-tet);* $(Meen)_2$; $(Eten)_2$; $(Pren)_2$; *(3,2,3-tet); (2,3,2-tet); (cyclam); and* $X = Br$, $N_4 \equiv (en)_2$; *(2,3,2-tet); (3,2,3-tet). The* $\Delta V^{\neq}$ *values for all the dichloro complexes, including* cis-$Co(en)_2Cl_2^+$ *averaged* -1.4 ± 1.0 cm^3 mol^{-1} *which was interpreted in terms of an* I_d *mechanism. The slightly more positive* $\Delta V^{\neq}$ *values for the dibromo species are also consistent with this mechanism. The aquation of the* trans-$Co(NH_3)_4CN(X)^+$ *complexes, where* $X = Cl$, *Br, I,* N_3 *and DMSO, was also considered to involve a similar mechanism, although in this case it possesses significantly more associative character.*

Introduction

A detailed re-examination of the steric course of the spontaneous and induced aquation of a number of (+)-*cis*-$Co(en)_2XY^{n+}$ complexes by Jackson and Sargeson [1] refuted the previously accepted generalization that *cis* complexes aquate with retention of configuration. Indeed the aquation of both *cis* and *trans* isomers involves stereochemical change, although the products formed from each isomer do not contain the same isomeric ratio. Additional evidence was presented for a similarity in the steric course of spontaneous and induced aquation involving a common intermediate of reduced coordination number. One sensitive mechanistic probe used by these authors was to determine the competition ratios for added nucleophiles.

The volume of activation provides independent information as to the nature of the reaction mechanism as evident from an earlier investigation [2] of the aquation of a series of $Co(NH_3)_5X^{n+}$ complexes from which it was concluded that dissociation of the leaving group was virtually complete in the transition state. This also serves to substantiate the findings of Jackson and Sargeson [1].

High pressure kinetic studies of the water exchange [3] and isomerization [4] of *trans*-$Co(en)_2(OH_2)_2^{3+}$ provided strong evidence for two distinct mechanisms with a tetragonal pyramidal intermediate being produced in the former reaction, while in the latter process a trigonal bipyramidal intermediate is involved. In the light of these conclusions and those discussed above it is of interest to see to which, if either, group the aquation reactions belong.

Moreover, complexes of this type also provide an opportunity to vary the amine ligands in a systematic manner in order to gauge their effect on the volume of activation. In other words, how sensitive is this parameter to structural modifications within the substrate?

Experimental

Materials

The following complexes were prepared and purified by standard methods: *trans*-dichlorotetraamminecobalt(III) chloride, *trans*-$[Co(NH_3)_4Cl_2]Cl$ [5]; *trans*-dichlorobisethylenedimainecobalt(III)-chloride, *trans*-$[Co(en)_2Cl_2]Cl$ [6, 7]; *cis*-dichlorobisethylenediaminecobalt(III) chloride, *cis*-$[Co(en)_2Cl_2]Cl$ [7]; *trans*-dichlorobis(N-methylethylenediamine)cobalt(III)chloride·hydrochloride, *trans*-$[Co(Meen)_2Cl_2]Cl\cdot HCl$ [8]; *trans*-dichlorobis(N-ethylethylenediamine)cobalt(III)chloride·hydrochloride, *trans*-$[Co(Eten)_2Cl_2]Cl\cdot 1.5HCl$ [8]; *trans*-dichlorobis(N-propylethylenediamine)cobalt(III)-chloride·hydrochloride, *trans*-$[Co(Pren)_2Cl_2]Cl\cdot 1.2HCl$ [8]; *trans*-dichloro(1,3-bis-(2′-aminoethylamino)propanecobalt(III) chloride, *trans*-$[Co(2,3,2\text{-}tet)Cl_2]Cl$ [9]; *trans*-RR,SS-dichloro(N,N′-bis-(3-aminopropyl)ethylenediamine)cobalt(III) chloride,

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TABLE I. Apparent Molar Volumes of $[CoN_4XY]Z$ Complexes and their Constituent Ions.

Complex	Temperature °C	ϕ $cm^3\ mol^{-1}$	Complex Ion	ϕ^a $cm^3\ mol^{-1}$
trans-$[Co(NH_3)_4Cl_2]Cl$	10	112.8 ± 0.5	*trans*-$[Co(NH_3)_4Cl_2]^+$	91.1
trans-$[Co(en)_2Cl_2]Cl$	25, 30	158.4 ± 0.8	*trans*-$[Co(en)_2Cl_2]^+$	136.7
cis-$[Co(en)_2Cl_2]Cl$	25, 30	161.3 ± 0.7	*cis*-$[Co(en)_2Cl_2]^+$	139.5
trans-$[Cl(Meen)_2Cl_2]Cl$	30	174.7 ± 0.6	*trans*-$[Co(Meen)_2Cl_2]^+$	152.9
trans-$[Co(Eten)_2Cl_2]Cl$	30	200.3 ± 1.3	*trans*-$[Co(Eten)_2Cl_2]^+$	178.5
trans-$[Co(Pren)_2Cl_2]Cl$	30	232.4 ± 1.1	*trans*-$[Co(Pren)_2Cl_2]^+$	210.6
trans-$[Co(2,3,2\text{-tet})Cl_2]Cl$	30	196.9 ± 1.8	*trans*-$[Co(2,3,2\text{-tet})Cl_2]^+$	175.1
trans-R,S-$[Co(2,3,2\text{-tet})Cl_2]Cl$	25	195.8 ± 0.5	*trans*-R,S-$[Co(2,3,2\text{-tet})Cl_2]^+$	174.0
trans-RR,SS-$[Co(2,3,2\text{-tet})Cl_2]ClO_4$	25	216.2 ± 1.6	*trans*-RR,SS-$[Co(2,3,2\text{-tet})Cl_2]^+$	165.5
trans-$[Co(3,2,3\text{-tet})Cl_2]Cl$	30	215.2 ± 1.0	*trans*-$[Co(3,2,3\text{-tet})Cl_2]^+$	193.4
trans-$[Co(cyclam)Cl_2]Cl$	25	241.1 ± 0.6	*trans*-$[Co(cyclam)Cl_2]^+$	219.3
trans-$[Co(en)_2Br_2]Br$	30	180.2 ± 0.8	*trans*-$[Co(en)_2Br_2]^+$	150.8
trans-$[Co(2,3,2\text{-tet})Br_2]Br$	25, 30	211.5 ± 0.8	*trans*-$[Co(2,3,2\text{-tet})Br_2]^+$	182.1
trans-$[Co(3,2,3\text{-tet})Br_2]ClO_4$	30	241.9 ± 5.4	*trans*-$[Co(3,2,3\text{-tet})Br_2]^+$	191.2
trans-$[Co(NH_3)_4CN(Cl)]Cl$	25	120.5 ± 0.4	*trans*-$[Co(NH_3)_4CN(Cl)]^+$	98.7
trans-$[Co(NH_3)_4CN(Br)]Br$	25	135.5 ± 1.1	*trans*-$[Co(NH_3)_4CN(Br)]^+$	106.1
trans-$[Co(NH_3)_4CN(I)]I$	25	157.2 ± 3.0	*trans*-$[Co(NH_3)_4CN(I)]^+$	116.2
trans-$[Co(NH_3)_4CN(N_3)]N_3$	25	132.2 ± 0.4	*trans*-$[Co(NH_3)_4CN(N_3)]^+$	100.4
trans-$[Co(NH_3)_4CN(OH_2)]Cl_2$	25	125.9 ± 0.5	*trans*-$[Co(NH_3)_4CN(OH_2)]^{2+}$	82.4

[a] Based on the assumption [2, 16], $\bar{V}(H^+) = -4.5\ cm^3\ mol^{-1}$, and the following individual ionic $\bar{V}$ values: Cl^-, 21.75; Br^-, 29.4; I^-, 41.0; ClO_4^-, 50.7; N_3^-, 31.8 $cm^3\ mol^{-1}$, $\bar{V}$(DMSO) [12] = 68.8 $cm^3\ mol^{-1}$.

trans-RR,SS-$[Co(3,2,3\text{-tet})Cl_2]Cl$* [10]; *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III)chloride, *trans*-$[Co(cyclam)Cl_2]Cl$ [11]; *trans*-dibromobisethylenediaminecobalt(III) bromide, *trans*-$[Co(en)_2Br_2]Br$ [12]; *trans*-RR,SS-dibromo-(N,N′-bis(3-aminopropyl)ethylenediamine)cobalt(III)-perchlorate, *trans*-RR,SS-$[Co(3,2,3\text{-tet})Br_2]ClO_4$ [10]; *trans*-cyanoaquotetraamminecobalt(III) chloride, *trans*-$[Co(NH_3)_4CN(OH_2)]Cl_2$ [13]; *trans*-cyanochlorotetraamminecobalt(III) chloride, *trans*-$[Co(NH_3)_4CN(Cl)]Cl$ [14]; *trans*-cyanobromotetraamminecobalt(III)bromide, *trans*-$[Co(NH_3)_4CN(Br)]$-Br [14]; *trans*-cyanoiodotetraamminecobalt(III)-iodide, *trans*-$[Co(NH_3)_4CN(I)]I$ [14]; *trans*-cyano-azidotetraamminecobalt(III)acide, *trans*-$[Co(NH_3)_4CN(N_3)]N_3$ [14].

Trans-cyanodimethylsulfoxidetetraamminecobalt-(III)perchlorate was synthesized by stirring a mixture of 2.42 g of *trans*$[Co(NH_3)_4CN(OH_2)]Cl_2$ and 4.5 g of $AgClO_4$ in 50 cm^3 DMSO for 2 hr at room temperature. The mixture was filtered and a total of 1–1.5 l of chloroform were added in small portions to the filtrate. The precipitate was filtered off, washed with chloroform and ether, then dried for several hours under vacuum. *Anal.* Calcd. for *trans*-$[Co(NH_3)_4CN(DMSO)](ClO_4)_2$: C, 7.7; H, 4.2; N, 16.3; Cl, 16.5. Found: C, 8.4; H, 4.2; N, 16.2; Cl, 16.9%.

All of the above compounds were analyzed to ensure their purity. Their spectra were recorded on a Zeiss DMR 10 spectrophotometer and compared with the spectra reported in the literature.

Kinetics

The pressure dependencies of all the reactions were followed *in situ* with a Zeiss PMQ II spectrophotometer modified to include a split beam arrangement for greater stability. The pressure vessel and the quartz cell contained therein have been described previously [15]. The temperature inside the vessel was controlled to within ±0.1 °C.

The majority of the temperature dependent studies at normal pressure were conducted in a Cary 14 instrument using a thermostatted, programmable cell changer containing up to five 1 cm quartz cells. The slow reaction of *trans*-$Co(NH_3)_4CN(I)^+$ at higher pH values was monitored by sampling a thermostatted solution and recording the absorbance at 361 nm.

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*A large sample of this complex and *trans*-R,S-$[Co(2,3,2\text{-tet})Cl_2]Cl$ were provided by M. L. Tobe.

TABLE II. Apparent Molar Volumes of $[CoN_4X(OH_2)]X_2$ Aquation Products and the Complex Cations at 25 °C.

Complex	ϕ cm^3 mol^{-1}	Complex Cation	ϕ^a cm^3 mol^{-1}
$[Co(NH_3)_4Cl(OH_2)]Cl_2$	115.3 ± 1.6	$Co(NH_3)_4Cl(OH_2)^{2+}$	71.8
$[Co(en)_2Cl(OH_2)]Cl_2$	162.5 ± 0.9	$Co(en)_2Cl(OH_2)^{2+}$	119.0
$[Co(en)_2Cl(OH_2)]Cl_2{}^b$	165.0 ± 1.1	$Co(en)_2Cl(OH_2)^{2+}$	121.5
$[Co(Meen)_2Cl(OH_2)]Cl_2$	179.5 ± 0.2	$Co(Meen)_2Cl(OH_2)^{2+}$	136.0
$[Co(Eten)_2Cl(OH_2)]Cl_2$	206.5 ± 0.5	$Co(Eten)_2Cl(OH_2)^{2+}$	163.0
$[Co(Pren)_2Cl(OH_2)]Cl_2$	235.4 ± 0.5	$Co(Pren)_2Cl(OH_2)^{2+}$	191.9
$[Co(2,3,2\text{-tet})Cl(OH_2)]Cl_2$	200.6 ± 1.6	$Co(2,3\text{-}2\text{-tet})Cl(OH_2)^{2+}$	157.1
$[Co(3,2,3\text{-tet})Cl(OH_2)]Cl_2$	218.2 ± 1.7	$Co(3,2,3\text{-tet})Cl(OH_2)^{2+}$	174.7
$[Co(cyclam)Cl(OH_2)]Cl_2$	244.7 ± 0.6	$Co(cyclam)Cl(OH_2)^{2+}$	201.2
$[Co(en)_2Br(OH_2)]Br_2$	183.7 ± 0.9	$Co(en)_2Br(OH_2)^{2+}$	124.9
$[Co(2,3,2\text{-tet})Br(OH_2)]Br_2$	216.4 ± 1.5	$Co(2,3,2\text{-tet})Br(OH_2)^{2+}$	157.6

[a] Calculated on the assumption [2, 16], $\bar{V}(Cl^-) = 21.75$ cm^3 mol^{-1} and $\bar{V}(Br^-) = 29.4$ cm^3 mol^{-1}. [b] Substrate was *cis*-$[Co(en)_2Cl_2]Cl$; the remainder were trans.

Density Measurements

The densities of the various solutions were measured using a digital densimeter, Anton Paar DMA 02, which was thermostatted to within ±0.002 °C. A range of concentrations was investigated for each complex and the calculated apparent molar volumes were averaged because they proved to be independent of concentration. The mean ϕ_i values are presented in Table I.

The aquation reactions were also monitored by this technique by taking aliquots from a bulk solution of the complex at time intervals of up to one week using three such solutions, each at different concentrations, for each complex. This provided a method for determining the apparent molar volumes of the final products and these values are listed in Table II.

IR Measurements

The FIR spectra were recorded on a Beckman IR 720 spectrometer. The samples were ground to a paste in Nujol, then pressed between two polyethylene plates. The spectrum of each sample was measured at least twice to guard against possible decomposition of the complex and any changes in the optical system. Four samples of each complex were taken.

Results

The overall reaction scheme for the dihalogeno complexes in acidic solution can be represented by the following equations:

These reactions were only followed until the slower second aquation step became a factor. In addition, a wavelength was chosen to monitor them where either the *cis*- and *trans*-$CoN_4X(OH_2)^{2+}$ species exhibit an isosbestic point or where their molar extinction coefficients are so similar that isomerization did not affect the rate plots. These wavelengths are shown in parentheses in Table III. Thus, the appearance of the ultimate diaquo products could be detected by observing any departure from the initial isosbestic points so that for this purpose it was necessary to run complete spectral scans as a function of time for each new reaction.

The rate constants were calculated from the initial slopes of plots of $\ln(A_p - A_t)$ *versus* t, where A_p is the calculated absorbance of the $CoN_4X(OH_2)^{2+}$ species and A_t is the absorbance at time t. In the case of the reaction involving *trans*-$Co(cyclam)Cl_2^+$ the calculation of A_p required a knowledge of the aquation equilibrium constant [11], whereas for all the remaining dihalogeno complexes A_p was obtained by a back-extrapolation to t = 0 of the second branch of A_t *versus* time. Naturally, in the series of complexes, *trans*-$Co(NH_3)_4CN(X)^+$, A_p could be directly measured from the aquo complex.

The close agreement between the rate constants obtained in this study and those obtained by titration of the liberated halide (this method is particularly sensitive to the advent of secondary aquation, but is independent of isomerization) provides independent evidence that the rate constants reported here refer exclusively to the loss of the first halide [17–20].

$$\begin{tikzcd}
 & cis\text{-}CoN_4X(OH_2)^{2+} \arrow[r] \arrow[dd, shift left] & cis\text{-}CoN_4(OH_2)_2^{3+} \arrow[dd, shift left] \\
cis\text{- or } trans\text{-}CoN_4X_2^+ \arrow[ur] \arrow[dr] & & \\
 & trans\text{-}CoN_4X(OH_2)^{2+} \arrow[r] \arrow[uu, shift left] & trans\text{-}CoN_4(OH_2)_2^{3+} \arrow[uu, shift left]
\end{tikzcd} \qquad (1)$$

TABLE III. Temperature Dependence of k_{obs}.

Complex	μ	Temperature, °C	10^5 k_{obs} s^{-1}
trans-[Co(NH_3)$_4$$Cl_2$]Cl (253 nm)	*ca.* 0	10.0	23.7 ± 0.5
		15.0	50.5 ± 1.0
		20.0	111 ± 1
		25.0	227 ± 12
		30.0	421 ± 8
trans-[Co(en)$_2$$Cl_2$]Cl (301, 530 nm)	*ca.* 0	30.4	7.1 ± 1.4
		34.5	12.2 ± 1.2
		39.4	23.1 ± 5.6
		44.3	45.6 ± 6.0
		50.5	85.8 ± 10.3
trans-[Co(2,3,2-tet)Cl_2]Cl (306 nm)	*ca.* 0	20.0	0.88 ± 0.04
		30.0	3.71 ± 0.30
		35.0	7.91 ± 0.15
		40.0	14.3 ± 0.8
		45.0	34.2 ± 5.4
		50.0	61.5 ± 2.4
trans-[Co(NH_3)$_4$$Cl_2$]Cl	1 *M*, ($NaClO_4$)	10.0	16.8 ± 0.8
		15.0	32.3 ± 1.9
		20.0	66.8 ± 3.9
		25.0	134 ± 5
		30.0	236 ± 1
		35.0	434 ± 8
trans-[Co(en)$_2$$Cl_2$]Cl	1 *M*, ($NaClO_4$)	30.0	4.87 ± 0.04
		35.0	10.7 ± 0.5
		40.0	21.2 ± 1.0
		45.0	41.6 ± 2.0
		50.0	77.3 ± 2.2
		55.0	161 ± 7
trans-[Co(2,3,2-tet)Cl_2]Cl	1 *M*, ($NaClO_4$)	35.0	4.85 ± 0.40
		40.0	10.4 ± 2.9
		45.0	22.0 ± 3.6
		50.0	38.5 ± 2.2
		55.0	70.4 ± 1.9
trans-[Co(NH_3)$_4$$Cl_2$]Cl	0.01 *M*, HNO_3 0.1 *M*, $NaClO_4$	10.0	31.7 ± 4.0
		15.0	63.4 ± 3.3
		20.0	111 ± 10
		25.0	224 ± 6
		30.0	380 ± 10
cis-[Co(en)$_2$$Cl_2$]Cl (310 nm)	0.01 *M*, HNO_3 0.1 *M*, $NaClO_4$	25.0	25.4 ± 1.7
		30.0	43.4 ± 2.0
		35.0	88.1 ± 4.9
		40.0	174 ± 3
		45.0	248 ± 6
		50.0	406 ± 10
trans-[Co(en)$_2$$Cl_2$]Cl	0.01 *M*, HNO_3 0.1 *M*, $NaClO_4$	30.0	7.70 ± 0.20
		35.0	14.6 ± 0.2
		40.0	28.6 ± 1.1
		45.0	59.5 ± 2.0
		50.0	129 ± 8

(continued on facing page)

TABLE III. *(continued)*

Complex	μ	Temperature, °C	10^5 k_{obs} s^{-1}
		55.0	228 ± 29
trans-$[Co(Meen)_2Cl_2$	0.01 *M*, HNO_3	25.0	1.59 ± 0.06
(305 nm)	0.1 *M*, $NaClO_4$	30.0	3.36 ± 0.04
		35.0	6.31 ± 0.14
		40.0	13.0 ± 0.5
		45.0	26.9 ± 0.4
		50.0	57.3 ± 2.4
trans-$[Co(Eten)_2Cl_2]Cl$	0.01 *M*, HNO_3	25.0	8.12 ± 0.27
(312 nm)	0.1 *M*, $NaClO_4$	30.0	15.8 ± 0.6
		35.0	29.7 ± 1.3
		40.0	52.4 ± 2.8
		45.0	89.1 ± 7.7
		50.0	179 ± 9
trans-$[Co(Pren)_2Cl_2]Cl$	0.01 *M*, HNO_3	25.0	7.25 ± 0.12
(313 nm)	0.1 *M*, $NaClO_4$	30.0	13.7 ± 0.6
		35.0	30.6 ± 2.5
		40.0	66.5 ± 3.2
trans-$[Co(2,3,2\text{-tet})Cl_2]Cl$	0.01 *M*, HNO_3	25.0	1.24 ± 0.11
	0.1 *M*, $NaClO_4$	40.0	9.05 ± 0.49
		45.0	17.4 ± 0.5
		50.0	32.7 ± 1.2
		55.0	63.3 ± 5.4
trans-$[Co(3,2,3\text{-tet})Cl_2]Cl$	0.01 *M*, HNO_3	30.0	11.3 ± 1.1
(308 nm)	0.1 *M*, $NaClO_4$	35.0	21.5 ± 6.3
		40.0	39.6 ± 7.5
		45.0	86.9 ± 6.2
		50.0	157 ± 37
trans-$[Co(en)_2Br_2]Br$	0.01 *M*, HNO_3	25.0	15.0 ± 1.3
(490, 351 nm)	01. *M*, $NaClO_4$	30.0	30.4 ± 2.2
		35.0	58.2 ± 4.3
		40.0	105 ± 7
trans-$[Co(2,3,2\text{-tet})Br_2]Br$	0.01 *M*, HNO_3	25.0	11.4 ± 1.1
(351 nm)	0.1 *M*, $NaClO_4$	30.0	23.4 ± 0.9
		35.0	45.4 ± 1.4
		40.0	76.2 ± 7.1
		45.0	156 ± 3
trans-$[Co(3,2,3\text{-tet})Br_2]ClO_4$	0.01 *M*, HNO_3	25.0	54.1 ± 2.3
(353 nm)	0.1 *M*, $NaClO_4$	30.0	104 ± 3
		35.0	203 ± 10
trans-$[Co(NH_3)_4CN(Cl)]Cl$	0.01 *M*, HNO_3	30.0	2.01 ± 0.13
(296 nm)	0.1 *M*, $NaClO_4$	35.0	3.05 ± 0.12
		40.0	5.51 ± 0.21
		45.0	8.30 ± 0.35
		50.0	13.7 ± 0.6
trans-$[Co(NH_3)_4CN(Br)]Br$	0.01 *M*, HNO_3	25.0	4.37 ± 0.26
(300 nm)	0.1 *M*, $NaClO_4$	30.0	6.84 ± 0.59
		35.0	10.6 ± 0.2

(continued overleaf)

TABLE III. *(continued)*

Complex	μ	Temperature, °C	10^5 k_{obs} s^{-1}
		40.0	17.3 ± 0.4
		45.0	26.0 ± 0.4
		50.0	37.9 ± 0.4
trans-$[Co(NH_3)_4CN(I)]I$	0.01 *M*, HNO_3	25.0	5.87 ± 0.32
(361 nm)	0.1 *M*, $NaClO_4$	30.0	11.1 ± 0.9
		35.0	17.5 ± 0.7
		40.0	41.1 ± 2.6
		45.0	71.8 ± 2.7
		50.0	127 ± 2
trans-$[Co(NH_3)_4CN(N_3)]N_3$	0.1 *M* HNO_3	25.0	1.01 ± 0.04
		30.0	2.08 ± 0.18
		35.0	4.12 ± 0.06
		40.0	6.85 ± 0.19
		45.0	12.1 ± 0.4
		50.0	21.7 ± 1.0

TABLE IV. Pressure Dependence of k_{obs}.

Complex (Pressure, MPa)	μ	$[H^+]$ *M*	t °C	10^5 k_{obs} (s^{-1})						
				0.1	25.3	50.7	76.0	101.3	126.7	152.0
trans-$[Co(NH_3)_4Cl_2]Cl^a$	0	–	25	227	231	243	241	244		250
trans-$[Co(en)_2Cl_2]Cl$	0	–	25	3.22	3.49	3.73	3.84	3.68		3.63
trans-$[Co(2,3,2\text{-tet})Cl_2]Cl$	0	–	50	61.5	61.8	62.3	64.6	63.9		
	1	–	50	38.5	38.5	39.8	41.0	40.8		
trans-$[Co(NH_3)_4Cl_2]Cl$	0.1	0.01	10	30.7	30.4	34.0	33.2	33.2	35.2	33.4
cis-$[Co(en)_2Cl_2]Cl$	0.1	0.01	30	43.1	45.9	44.8	44.3	45.2	44.3	45.1
trans-$[Co(en)_2Cl_2]Cl$	0.1	0.01	30	5.96	6.71	6.74	6.96	6.85	6.70	6.56
trans-$[Co(Meen)_2Cl_2]Cl$	0.1	0.01	30	3.19	3.28	3.26	3.44	3.72	3.70	3.77
trans-$[Co(Eten)_2Cl_2]Cl$	0.1	0.01	30	15.9	17.6	16.7	18.3	17.3	16.5	16.9
trans-$[Co(Pren)_2Cl_2]Cl$	0.1	0.01	30	14.4	14.3	14.3	15.2	14.1	13.8	14.1
trans-$[Co(2,3,2\text{-tet})Cl_2]Cl$	0.1	0.01	30	2.55	2.67	2.74	2.75	2.74	2.75	2.74
trans-$[Co(3,2,3\text{-tet})Cl_2]Cl$	0.1	0.01	30	11.3	11.1	13.5	13.8	13.8	13.1	13.0
trans-$[Co(cyclam)Cl_2]Cl^b$	0.1	0.1	50	3.39		3.28		3.61		3.74
trans-$[Co(en)_2Br_2]Br$	0.1	0.01	30	30.4	30.0	27.4	28.1	28.3	27.7	27.8
trans-$[Co(2,3,2\text{-tet})Br_2]Br$	0.1	0.01	30	23.4	22.8	23.1	20.7	20.0	20.2	19.4
trans-$[Co(NH_3)_4CN(Cl)]Cl$	0.1	0.01	40	5.61	6.15	6.75	7.20	7.57	7.97	8.76
trans-$[Co(NH_3)_4CN(Br)]Br$	0.1	0.01	40	17.4	17.7	20.3	21.3	22.8	23.8	24.2
trans-$[Co(NH_3)_4CN(I)]I$	0.1	0.01	30	11.2	11.4	12.0	12.5	13.1	12.1	14.2
trans-$[Co(NH_3)_4CN(N_3)]N_3$	0.1	0.1	40	6.85	6.56	6.16	5.94	5.53	5.22	4.94
trans-$[Co(NH_3)_4CN(DMSO)](ClO_4)_2{}^c$	0.1	0.01	20	140	136	131	134	135	132	133

[a] Additional 10^5 k_{obs} values: 235 (10.1). 233 (20.3); 243(30.4); and 240 s^{-1} (40.5 MPa). [b] Monitored at 310 nm. [c] Monitored at 275 nm.

A linear least squares program was used to fit all the $\ln(A_p - A_t)/t$ data. When these plots proved to be curved the program would automatically continue to delete the last value of A_t until a constant value of k_{obs} was obtained. Nevertheless, such plots were generally linear for at least three half-lives.

TABLE V. Summary of Rate Constants, Activation Parameters and Volumes of Reaction.

Complex	10^5 k (25 °C) s^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}	$\Delta V^{\neq}$ (t, °C) cm^3 mol^{-1}	$\Delta\bar{V}$ cm^3 mol^{-1}
trans-$[Co(NH_3)_4Cl_2]Cl^a$	227	101.2 ± 1.7	44 ± 6	−1.3 ± 0.3(25)	−15.5 ± 2.1
^{b}	134	92.7 ± 1.2	10 ± 4		
^{c}	224	86.6 ± 1.9	−6 ± 7	−1.7 ± 0.7(10)	
trans-R,S-$[Co(2,3,2\text{-}tet)Cl_2]Cl^a$	1.7	109.8 ± 2.4	32 ± 8	−1.3 ± 0.4(50)	−13.1 ± 2.1
^{b}	1.2	111.2 ± 1.5	39 ± 5	−1.9 ± 0.4(50)	
^{c}	1.2	103.5 ± 1.4	8 ± 4	−1.0 ± 0.4(30)	
trans-$[Co(en)_2Cl_2]Cl^a$	3.4	99.9 ± 2.4	5 ± 8	−1.7 ± 1.1(25)	−13.9 ± 1.7
^{b}	2.2	109.4 ± 3.4	28 ± 11		
^{c}	3.2	111.8 ± 2.6	44 ± 8	−1.1 ± 0.9(30)	
cis-$[Co(en)_2Cl_2]Cl^c$	25.4	88.1 ± 3.8	−18 ± 12	−0.3 ± 0.4(30)	−14.2 ± 1.8
trans-$[Co(Meen)_2Cl_2]Cl^c$	1.59	113.3 ± 2.4	36 ± 8	−3.1 ± 0.5(30)	−13.1 ± 0.8
trans-$[Co(Eten)_2Cl_2]Cl^c$	8.12	94.5 ± 1.8	−6 ± 6	−0.3 ± 0.9(30)	−11.7 ± 1.8
trans-$[Co(Pren)_2Cl_2]Cl^c$	7.25	113.1 ± 5.2	55 ± 17	+0.3 ± 0.6(30)	−14.9 ± 1.6
trans-$[Co(3,2,3\text{-}tet)Cl_2]Cl^c$	5.6	106.1 ± 3.1	29 ± 10	−2.8 ± 1.5(30)	−14.9 ± 2.7
trans-$[Co(cyclam)Cl_2]Cl^d$	0.14^e	76.5^e	-25^e	−2.0 ± 0.9(50)	−14.3 ± 1.2
trans-RR,SS-$[Co(2,3,2\text{-}tet)Cl_2]Cl^f$		108.3^e	50^e	+1.0 ± 0.4(25)	
trans-R,S-$[Co(2,3,2\text{-}tet)Cl_2]Cl^f$				−0.8 ± 1.7(25)	
trans-$[Co(en)_2Br_2]Br^c$	15.0	98.0 ± 1.9	11 ± 6	+1.4 ± 0.6(30)	−14.5 ± 1.7
trans-$[Co(2,3,2\text{-}tet)Br_2]Br^c$	11.4	98.6 ± 2.8	11 ± 9	+3.4 ± 0.6(30)	−13.1 ± 2.3
trans-$[Co(3,2,3\text{-}tet)Br_2]Br^c$	54.1	98.4 ± 1.6	23 ± 5		
trans-$[Co(NH_3)_4CN(Cl)]Cl^c$	1.15	76.2 ± 2.5	−84 ± 8	−7.3 ± 0.4(40)	−12.5 ± 0.9
trans-$[Co(NH_3)_4CN(Br)]Br^c$	4.37	67.5 ± 0.9	−102 ± 3	−6.2 ± 0.6(40)	−12.3 ± 1.6
trans-$[Co(NH_3)_4CN(I)]I^c$	5.87	97.3 ± 3.6	0 ± 12	−3.3 ± 0.9(30)	−10.8 ± 3.5
trans-$[Co(NH_3)_4CN(N_3)]N_3{}^d$	1.01	94.1 ± 2.0	−23 ± 7	+5.7 ± 0.2(40)	
trans-$[Co(NH_3)_4CN(DMSO)](ClO_4)_2{}^c$	140(20)			+0.6 ± 0.3(20)	

$^a\mu \sim 0$. $^b\mu = 1$ $(NaClO_4)$. $^c[H^+] = 0.01$ *M* (HNO_3); $\mu = 0.1$ $(NaClO_4)$. $^d[H^+] = \mu = 0.1$ *M* (HNO_3). ^{e}References 22, 23 and $\mu \sim [H^+] = 0.01$ *M* (HNO_3).

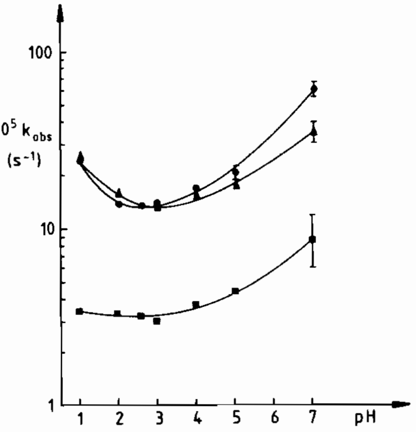

Fig. 1. pH Dependence of k_{obs} at 30 °C; $[HNO_3] = 0.01$ *M*; $\mu = 0.1$ $(NaClO_4)$: ■ *trans*-$[Co(Meen)_2Cl_2]Cl$; ▲ *trans*-$[Co(Eten)_2Cl_2]Cl$; ● *trans*-$[Co(Pren)_2Cl_2]Cl$.

Table III lists the observed first-order rate constants as a function of temperature and, in some cases, ion strength and/or acidity. Similarly, in Table IV k_{obs} is given as a function of pressure, and to a limited extent, ionic strength. The plots of ln k_{obs} *versus* pressure were linear within the range studied and were therefore treated with a linear least squares program. However, the slopes, or $\Delta V^{\neq}$ values, are generally so small that over the pressure range 1 to 1300 bar it would be extremely difficult to detect any curvature.

The activation parameters are summarized in Table V.

A variation in pH from 1.00 to 7.00 had no effect on the observed rate constants for the aquation of *trans*-$Co(NH_3)_4Cl_2^+$, *cis*-$Co(en)_2Cl_2^+$, *trans*-$Co(en)_2Cl_2^+$ or *trans*-$Co(en)_2Br_2^+$ at 30 °C and $\mu = 0.1$ $(NaClO_4)$. The mean values of k_{obs} calculated from the measured values at each integer pH value in this range are $(3.8 \pm 0.2) \times 10^{-3}$ s^{-1}, $(4.33 \pm 0.07) \times 10^{-4}$ s^{-1}, $(7.0 \pm 0.5) \times 10^{-5}$ s^{-1}, and $(3.03 \pm 0.08) \times 10^{-4}$ s^{-1}, respectively. On the other hand, the pH dependence of k_{obs} for the trans-dichloro complexes of $(Meen)_2$, $(Eten)_2$ and $(Pren)_2$ showed definite minima as can be seen from Fig. 1, while the k_{obs} values are

TABLE VI. Assigned Frequencies in the I.R. Spectrum of trans[CoN_4X_2]Y Complexes.

trans-Complex	Code[a]	δ (N–Co–N) cm^{-1}	ν (Co–Cl) cm^{-1}
[$Co(tmd)_2Cl_2$]ClO_4	1	260[b]	362[b]
[$Co(sbn)_2Cl_2$]ClO_4	2	272[b]	350[b]
[$Co(ibn)_2Cl_2$]ClO_4	3	275[b]	350[b]
[$Co(NH_3)_4Cl_2$]Cl	4	290[b]	353[b]
[$Co(NH_3)_4Cl_2$]Cl	5	290 ± 1	352 ± 1
[$Co(pn)_2Cl_2$]ClO_4	6	291[b]	
[$Co(en)_2Cl_2$]ClO_4	7	295[b]	358[b]
[$Co(en)_2Cl_2$]Cl	8	294 ± 2	365 ± 1
[$Co(Meen)_2Cl_2$]Cl	9	295 ± 2	342 ± 1
[$Co(Eten)_2Cl_2$]Cl	10	291 ± 2	341 ± 1
[$Co(Pren)_2Cl_2$]Cl	11	291 ± 1	346 ± 1
[Co(2,3,2-tet)Cl_2]Cl	12	297[b]	345[b]
R,S-[Co(2,3,2-tet)Cl_2]Cl	13	298 ± 2	352 ± 1
			343 ± 1
R,S-[Co(2,3,2-tet)Cl_2]ClO_4	14	298 ± 2	352 ± 1
			343 ± 1
RR,SS-[Co(2,3,2-tet)Cl_2]ClO_4	15	282 ± 0.8	347 ± 1
[Co(3,2,3-tet)Cl_2]ClO_4	16	296[b]	351[b]
[Co(3,2,3-tet)Cl_2]Cl	17	292 ± 1	347 ± 1
[Co(cyclam)Cl_2]Cl	18	303 ± 1	340 ± 1
[$Co(en)_2Br_2$]ClO_4		281[b]	231[b]
[$Co(en)_2Br_2$]Br		301 ± 1	
[Co(3,2,3-tet)Br_2]ClO_4		285[b]	223[b]
[Co(3,2,3-tet)Br_2]ClO_4		283 ± 1	

[a] Code refers to Fig. 4. [b] Taken from reference 21.

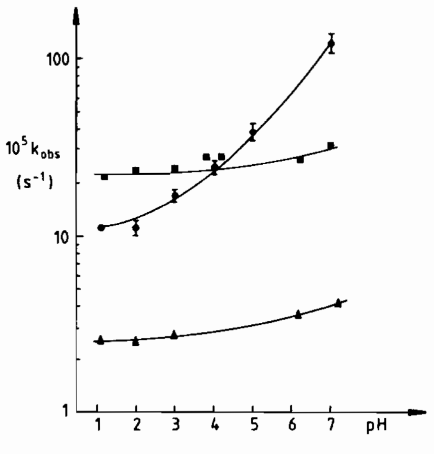

Fig. 2. pH Dependence of k_{obs} at 30 °C; [HNO_3] = 0.01 *M*; μ 0.1 ($NaClO_4$): ▲ *trans*-[Co(2,3,2-tet)Cl_2]Cl; ● *trans*-[Co(3,2,3-tet)Cl_2]Cl; ■ *trans*-[Co(2,3,2-tet)Br_2]Br.

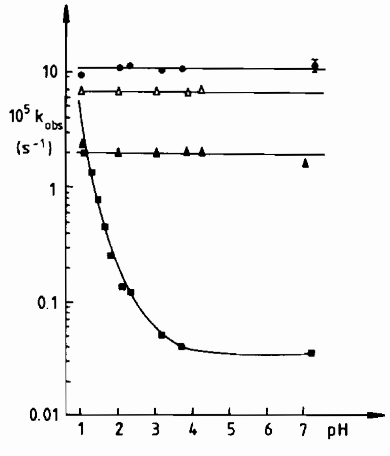

Fig. 3. pH Dependence of k_{obs} at 30 °C; [HNO_3] = 0.01 *M*; μ = 0.1 ($NaClO_4$): *trans*[$Co(NH_3)_4CN(X)$]X: ▲ X = Cl, △ X = Br; ● X = I; ■ x = N_3.

shown to increase with pH in Fig. 2 for the complex ions, *trans*-Co(2,3,2-tet)Cl_2^+, *trans*-Co(3,2,3-tet)Cl_2^+ and *trans*-Co(2,3,2-tet)Br_2^+ measured under the same conditions. Finally, for the series trans-$Co(NH_3)_4CN(X)^+$, k_{obs} is independent of pH for X = Cl, Br, and I, but decreases sharply to a minimum value for X = N_3 under these conditions, as illustrated in Fig. 3.

The assigned peaks in the FIR spectra of the *trans* complexes studied here are given in Table VI. They have been assigned [21] to the δ(N–Co–N) deformation vibration frequency and to the antisymmetric Co–X vibration. These data supplement the original spectral information catalogued by Eade, Bodley and House [21].

The δ(N–Co–N) peaks are characteristically steep on the lower wavenumber side, but are significantly flatter at higher wavenumbers indicating the existence of a small shoulder.

Discussion

At the present stage in the evolution of inorganic kinetics the mechanism for the aquation reactions of cobalt(III) complexes has been firmly established to be dissociative, although as indicated in the Introduction the degree of dissociation is still under discussion. It is with this understanding in mind that the following discussion is based.

From the accumulated data in Table V a number of correlations suggested in the past can be tested again. These include: an inverse relationship between the size of the amine ligand/s and the rate of aquation; a direct relationship between the length of the chelate ring/s and the reactivity of the complex; and a relationship between $\Delta S^{\neq}$ and the degree of stereochemical change in a reaction. Although this is not meant to imply that these correlations have not been critically examined previously [20, 24], it is relevant to reaffirm that the exceptions are numerous, especially in the first two cases. For the first three substrates in Table V, *trans*-$Co(NH_3)_4Cl_2^+$, *trans*-$Co(en)_2Cl_2^+$ and *trans*-Co(2,3,2-tet)Cl_2^+, for which no (or only slight) pH dependence of k_{obs} was observed, k_{obs} does tend to decrease with increasing ionic strength, but again no consistent trend is observable in either $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

Another correlation which encompasses the two relationships dealing with the size and chelate length of the amine ligands has been described by Eade, Rodley and House [21]. This concerns the flexibility of the overall molecule as it approaches the trigonal bipyramidal structure of the intermediate, and uses as a criterion the in-plane δ(N–Co–N) deformation mode. As can be clearly seen from the data in Table VI, this concept gives an explanation of the 2000 fold decrease in rate on going from the unhindered *trans*-$Co(NH_3)_4Cl_2^+$ complex to the tightly restrained structure of *trans*-Co-(cyclam)Cl_2^+. The relationship is shown to be quantitatively fulfilled in Fig. 4, which is merely an extension of the original graph of Eade *et al.* [21]. Despite the inherent difficulties in assigning these bands [21], the relationship is quite linear over a wide range of reactivities, except for the only monodentate case (N≡NH_3) which would anyway not be expected to conform as no steric restraints exist in the molecule. The ν(Co–Cl) values in Table VI confirm [21] that no similar relationship exists with k_{obs}. In particular, it is interesting to note that the difference between the more rigid structure of the R,S-(2,3,2-tet) ligand (the complex of which aquates with stereoretention) compared to RR,SS-(2,3,2-tet) (aquation also involves isomerization indicative of the greater flexibility of this coordinated ligand) is manifested in a 16 cm^{-1} shift in the δ(N–Co–N) frequency which in turn correlates perfectly with the difference in the rates of aquation of their parent complexes. The considerably larger $\Delta S^{\neq}$ value for *trans*-RR,SS-Co(2,3,2-tet)Cl_2^+ also attests to the larger change in the configuration of this amine chelate during the aquation reaction. This example further demonstrates that it is neither the size nor the length of the chelate rings which dictates the reactivity of the substrate, but rather the flexibility of the molecule as a whole.

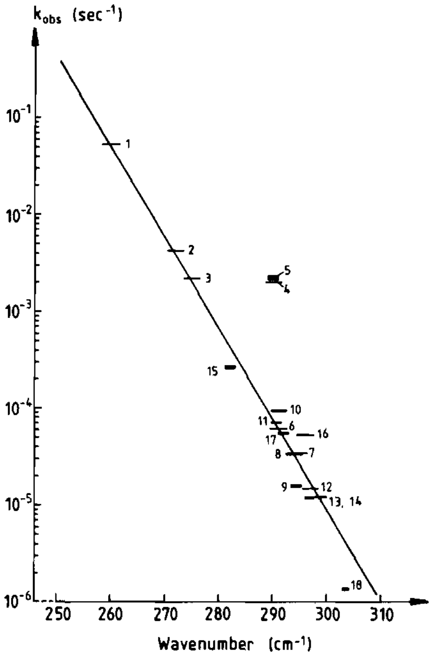

Fig. 4. k_{obs} as a function of the δ(N–Co–N) deformation frequency (see Table VI for the code).

Single N-substitution in the ethylenediamine ligand, as expected, has only a minor effect on the rate constant as it should not significantly influence the ease of rearrangement of the ligand.

Despite the large variations in the rates of aquation of the *trans*-$CoN_4X_2^+$ series, it is remarkable that the $\Delta V^{\neq}$ values remain un-influenced and virtually zero. There is a small trend towards more positive values for the bromo analogs, but this can be directly related to the larger size of the bromide ligand in that a larger volume is swept out as it dissociates from the substrate. Otherwise a mean value of -1.4 ± 1.0 cm^3 mol^{-1} virtually covers all the $\Delta V^{\neq}$ values for the nine dichloro complexes. This answers the question raised in the Introduction, *i.e.* at least for this series of complexes, the structure of the 'inert' amine ligand/s does not affect the volume of activation. This is understandable when one remembers that the primary volume change results from the extension of the Co–X bond and the associated solvent rearrangements, whereas rotational movements of the amine ligand do not contribute, although the latter will have a direct bearing on the energy of the system. Consequently, $\Delta V^{\neq}$ may be considered a less sensitive indicator of the reaction path, than $\Delta S^{\neq}$ for example, but at the same time it becomes a more readily interpretable parameter.

The constancy of $\Delta V^{\neq}$ reflects a common mechanism involving the same configurational changes during the formation of the transition state. As these reactions result in different ratios of *cis* and *trans*-$CoN_4X(OH_2)^{2+}$ products, it follows that isomerization occurs after the rate-determining dissociation of an X ligand. Alexander and Hamilton [20] also postulated that isomerization occurs as a rapid consecutive process.

Kruse and Taube [25] proposed that the isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ involved two intermediates, the first having a tetragonal pyramidal structure while the second, initiated by an out-of-plane δ(N–Co–N) vibration, takes the form of a trigonal bipyramid. The mechanism was considered to be either D or I_d. Meanwhile, $\Delta V^{\neq}$ for the water exchange reaction of *trans*-$Co(en)_2(OH_2)_2^{3+}$ was measured [26] at $+5.9 \pm 0.2$ cm^3 mol^{-1} with a compressibility of activation, $\Delta\beta^{\neq}$, ~0 cm^3 mol^{-1} kbar^{-1}, establishing conclusively that the mechanism is dissociative, probably of the I_d type. The water exchange process only involves the first intermediate. However, aquation of the *trans*-$CoN_4X_2^+$ complexes necessitates charge separation which is associated with increased electrostriction, and therefore a decrease in the volume of the system. Calculations of the contribution of electrostriction to $\Delta V^{\neq}$ using the Drude–Nernst equation [27] (the radii of the ions were determined from their molar volumes given in Table I) gave a mean value of -5.2 ± 0.3 cm^3 mol^{-1}. Thus the intrinsic volume change for the aquation of the dihalogeno complexes would be $(-1.4-(-5.2))$ or *ca.* 4 ± 1 cm^3 mol^{-1}, which is consistent with the formation of a tetragonal bipyramidal transition state. Moreover, $\Delta V^{\neq}$ for the isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ is significantly larger, +12.6 to +13.4 cm^3 mol^{-1} and strongly pressure dependent, $\Delta\beta^{\neq} = (0.9\text{–}11)$ cm^3 mol^{-1} kbar^{-1} depending on the nature and concentration of the supporting electrolyte [28]. These values were assumed to be consistent with the formation of a trigonal bipyramidal intermediate and therefore substantiate the original hypothesis of Kruse and Taube [25].

Lentz and Oh [29] reported a value of +11.0 cm^3 mol^{-1}, which was pressure dependent, for the spontaneous aquation of *trans*-$Co(en)_2Cl_2^+$ in obvious disagreement with our results. In addition, their value for $\Delta H^{\neq}$ of 64 kJ mol^{-1} is considerably smaller. One explanation of this discrepancy is that their data [29] refer to the *trans* to *cis* isomerization of $Co(en)_2Cl(OH_2)^{2+}$ as both $\Delta V^{\neq}$ and $\Delta H^{\neq}$ are similar to those reported for the isomerization of the diaquo species.

The overall volume change for the aquation reaction, $\Delta\bar{V}$, listed in Table V, was calculated from the volume data in Tables I and II and by assuming $\bar{V}(H_2O) = 18.0$ cm^3 mol^{-1}, according to the equation:

$$\Delta\bar{V} = \bar{V}\{CoN_4X(OH_2)^{2+}\} + \bar{V}\{X^-\} - \bar{V}\{CoN_4X_2^+\} - \bar{V}\{H_2O\} \quad (2)$$

Although the volumes in Table II strictly refer to a mixture of cis and trans isomers and not the actual initial product of aquation, the difference between the two isomers appears minimal (see for example the *cis*- and *trans*-$Co(en)_2Cl_2^+$ ions in Table I). The $\Delta\bar{V}$ values are also relatively constant over the whole range of amine ligands and seem independent of whether X = Cl or Br. The mean value is -13.9 ± 1.1 cm^3 mol^{-1}.

Unlike the $Co(NH_3)_5X^{n+}$ aquation reactions where $\Delta V^{\neq}$ and ΔV were quite similar [2] ($\Delta V^{\neq}$ was only 1 cm^3 mol^{-1} > $\Delta\bar{V}$), in the current system the volume of the transition state closely resembles that of the educt, *i.e.* $\Delta V^{\neq} \gg \Delta V$. This indicates that the negative contribution of Co–OH_2 bond formation is either entirely absent or very small in $\Delta V^{\neq}$ for the aquation of $CoN_4X_2^{2+}$ complexes. In other words, $(-13.9-(-1.4)) = 12.5 \pm 2.1$ cm^3 mol^{-1} represents the volume change associated with Co–OH_2 bond formation, which is in fact in reasonable agreement with the volume of a coordinated water molecule of 14 cm^3 mol^{-1}. Furthermore, this volume change should be independent of the nature of X and this is at least the case for X = Cl and Br. However, we are unable to explain the difference in the relative values of $\Delta V^{\neq}$ and $\Delta\bar{V}$ for the two otherwise similar systems, $Co(NH_3)_5X^{n+}$ and $CoN_4X_2^+$.

A final, and more controversial aspect of the $CoN_4X_2^+$ system deals with the use of 'model compounds' to predict the volume of the transition state species. The original concept was suggested by Stranks [30] who focussed on the example of $Ni(NH_3)_6^{2+}$ and $Ni(NH_3)_5^{2+}$ which he predicted would have equal volumes in solution to within 0.1 cm^3

mol^{-1}. Later we [2] endeavored to show that $\bar{V}\{Co(NH_3)_6^{3+}\}$ and $\bar{V}\{Co(NH_3)_5^{3+}\}$ were the same. However, Sisley and Swaddle [31] have recently criticized these findings. Certainly in the present system where the molecules are highly asymmetrical and can no longer be envisaged as rotating in a spherical cavity in the solvent, this relationship would not be expected to hold. The lower charges on the species cause them to more readily undergo expansion or contraction under pressure to different degrees. Nevertheless, the volume of a hypothetical five coordinate transition state, calculated from the expression, $\bar{V}\{CoN_4X^{2+}\} = \bar{V}\{CoN_4X_2^{+}\} + \Delta V^{\neq} - \bar{V}\{X\}$, is only slightly smaller than the corresponding values of $\bar{V}\{CoN_4X(OH_2)^{2+}\}$ by an average of 4.7 ± 2.0 cm^3 mol^{-1}. The difference would presumably be even smaller if $\bar{V}\{CoN_4X(OH_2)^{2+}\}$ could be measured for the pure trans-isomer, which may be of the order of 3 cm^3 mol^{-1} smaller than the value used here. Thus it would appear that a species, *trans*-$CoN_4X(NH_3)^{2+}$, might be a reasonable model for the five coordinate transition state in this system.

The order of the $\Delta V^{\neq}$s in Table V for the aquation of *trans*-$Co(NH_3)_4CN(X)^+$, where X = Cl, Br, I and DMSO respectively, reflect the increasing size of the leaving group in what must again be considered a basically dissociative process. The slightly positive $\Delta V^{\neq}$ for the latter reaction where no change in electrostriction occurs simply underlines this fact. From another perspective, calculation of $\bar{V}\{Co(NH_3)_4CN^{2+}\}$ from $(\bar{V}\{Co(NH_3)_4CN(X)^+\} + \Delta V^{\neq} - \bar{V}\{X\})$ for X = Cl, Br and I yields values of 69.6 ± 0.8, 70.5 ± 1.7 and 71.9 ± 3.9 cm^3 mol^{-1} respectively, which are similar enough to suggest a common transition state.

The accumulated errors in the $\Delta\bar{V}$ values given in Table V are rather large, but a similar treatment to that described above, *viz.* $\Delta\bar{V} - \Delta V^{\neq}$, still gives consistent values of −5.2 ± 1.3 (X = Cl), −6.1 ± 2.2 (X = Br) and −7.5 ± 4.4 cm^3 mol^{-1} (X = I) attributable to the residual shortening of the $Co{-}OH_2$ bond partially formed in the transition state. By comparison with the analogous value for the aquation of *trans*-$Co(NH_3)_4Cl_2^+$ of −13.8 cm^3 mol^{-1}, $Co{-}OH_2$ bond making in the transition state must be far more advanced for the cyano complexes. This is also compatible with the more negative $\Delta S^{\neq}$ values, at least for X = Cl and Br and with the general view of the inductive effects of a *trans* cyano ligand facilitating nucleophilic attack. Also the volume for the *trans*-$Co(NH_3)_4CN(OH_2)^{2+}$ cation given in Table I is significantly larger than those calculated above for the $\{Co(NH_3)_4CN, H_2O\}^{\neq}$ species.

The pressure dependence of the aquation of *trans*-$Co(NH_3)_4CN(N_3)^+$ was conducted at a pH = 1 where, as can be seen from Fig. 3, the reaction is substantially acid catalyzed and can be written as follows:

$$\textit{trans}\text{-}Co(NH_3)_4CN(N_3)^+ + H^+ \rightleftharpoons$$

$$\textit{trans}\text{-}Co(NH_3)_4CN(N_3H)^{2+} \qquad (3)$$

$$\xrightarrow{H_2O} \{[Co(NH_3)_4CN, H_2O]^{2+} + N_3H\}^{\neq} \qquad (4)$$

$$\rightarrow Co(NH_3)_4CN(OH_2)^{2+} + N_3H \qquad (5)$$

such that the measured $\Delta V^{\neq}$ is a composite quantity involving eqns. (3) and (4)

$$\Delta V^{\neq} = \bar{V}\{Co(NH_3)_4CN, H_2O^{2+}\} + \bar{V}\{N_3H\} -$$

$$- \bar{V}\{\text{trans-}Co(NH_3)_4CN(N_3)^+\} - \bar{V}\{H^+\} \qquad (6)$$

Using a similar treatment of the volume data for the acid-catalyzed aquation of $Co(CN)_5N_3^{3-}$ [32], a value of 32.5 ± 2.1 cm^3 mol^{-1} for $\bar{V}\{N_3H\}$ can be taken. Thus eqn. (6) gives,

$$\Delta V^{\neq}_{calc} = 70.7 + 32.5 - 100.4 + 4.5 = +7.3\ cm^3\ mol^{-1} \qquad (7)$$

which is in excellent agreement with the experimental value of +5.7 cm^3 mol^{-1} considering the number of measured quantities involved in the calculation.

Finally, from the value of $\bar{V}\{N_3H\}$ a $\Delta\bar{V}$ for the overall reaction (eqns. 3 + 4 + 5) of +1.0 cm^3 mol^{-1} can be estimated such that $\Delta\bar{V} - \Delta\bar{V}^{\neq} = -4.7$ cm^3 mol^{-1}, which is consistent with the corresponding results for X = Cl, Br and I. All point to a common I_d mechanism. This substantiates the conclusion of Jackson and Sargeson [1] in so far as the acid catalyzed path is the same as the spontaneous one in terms of mechanism.

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References

1 W. G. Jackson and A. M. Sargeson, *Inorg. Chem., 17,* 1348 (1978).
2 D. A. Palmer and H. Kelm, *Inorg. Chem., 16,* 3139 (1977).
3 S. B. Tong, H. R. Krouse and T. W. Swaddle, *Inorg. Chem., 15,* 2643 (1976).
4 D. R. Stranks and N. Vanderhoek, *Inorg. Chem., 15,* 2639 (1976).
5 O. Glemser, 'Handbuch der präparativen anorganischen Chemie', G. Brauer, ed., Ferdinand Enke Verlag, Stuttgart, 1962, p. 1338.
6 S. C. Chan, *Aust. J. Chem., 20,* 595 (1967).
7 J. C. Bailar, Jr., *Inorg. Sunth., 2,* 222 (1947).

8 F. Basolo, *J. Am. Chem. Soc.*, *75*, 227 (1953).
9 H. G. Hamilton and M. D. Alexander, *Inorg. Chem.*, *5*, 2060 (1966).
10 B. Bosnich, J. MacB. Harrowfield and H. Boucher, *Inorg. Chem.*, *14*, 815 (1975).
11 B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem.*, *4*, 1102 (1965).
12 A. Werner, *Ann.*, *386*, 272 (1912).
13 H. Siebert, *Z. anorg. Chem.*, *327*, 63 (1964).
14 N. Maki, *Inorg. Chem.*, *13*, 2180 (1974).
15 F. K. Fleischmann, E. G. Conze, D. R. Stranks and H. Kelm, *Rev. Sci. Instrum.*, *45*, 1427 (1974).
16 R. A. Horne, Ed., 'Water and Aqueous Solutions: Structure, Thermodynamics and Transport Properties', Wiley–Interscience, London, 1972, Chapter 13.
17 R. G. Pearson, Ch. R. Boston and F. Basolo, *J. Am. Chem. Soc.*, *75*, 3089 (1953).
18 S. C. Chan, *J. Chem. Soc., A*, 418 (1965).
19 S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).
20 M. D. Alexander and H. G. Hamilton, *Inorg. Chem.*, *8*, 2131 (1969).
21 L. M. Eade, G. A. Rodley and D. A. House, *J. Inorg. Nucl. Chem.*, *37*, 1049 (1975).
22 R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, *8*, 1589 (1969).
23 C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 2069 (1967).
24 M. L. Tobe, *Inorg. Chem.*, *7*, 1260 (1968).
25 W. Kruse and H. Taube, *J. Am. Chem. Soc.*, *83*, 1280 (1961).
26 S. B. Tong, H. R. Krouse and T. W. Swaddle, *Inorg. Chem.*, *15*, 2643 (1976).
27 C. A. Eckert, *Ann. Revs. Phys. Chem.*, *23*, 339 (1972).
28 D. R. Stranks and N. Vanderhoek, *Inorg. Chem.*, *15*, 2639 (1976).
29 H. Lentz and S. O. Oh, *High Temp. High Pressures*, *7*, 91 (1975).
30 D. R. Stranks, *Pure Appl. Chem.*, *38*, 303 (1974).
31 M. J. Sisley and T. W. Swaddle, *Inorg. Chem.*, *20*, 2799 (1981).
32 D. A. Palmer and H. Kelm, *Z. anorg. allg. Chem.*, *450*, 50 (1979).